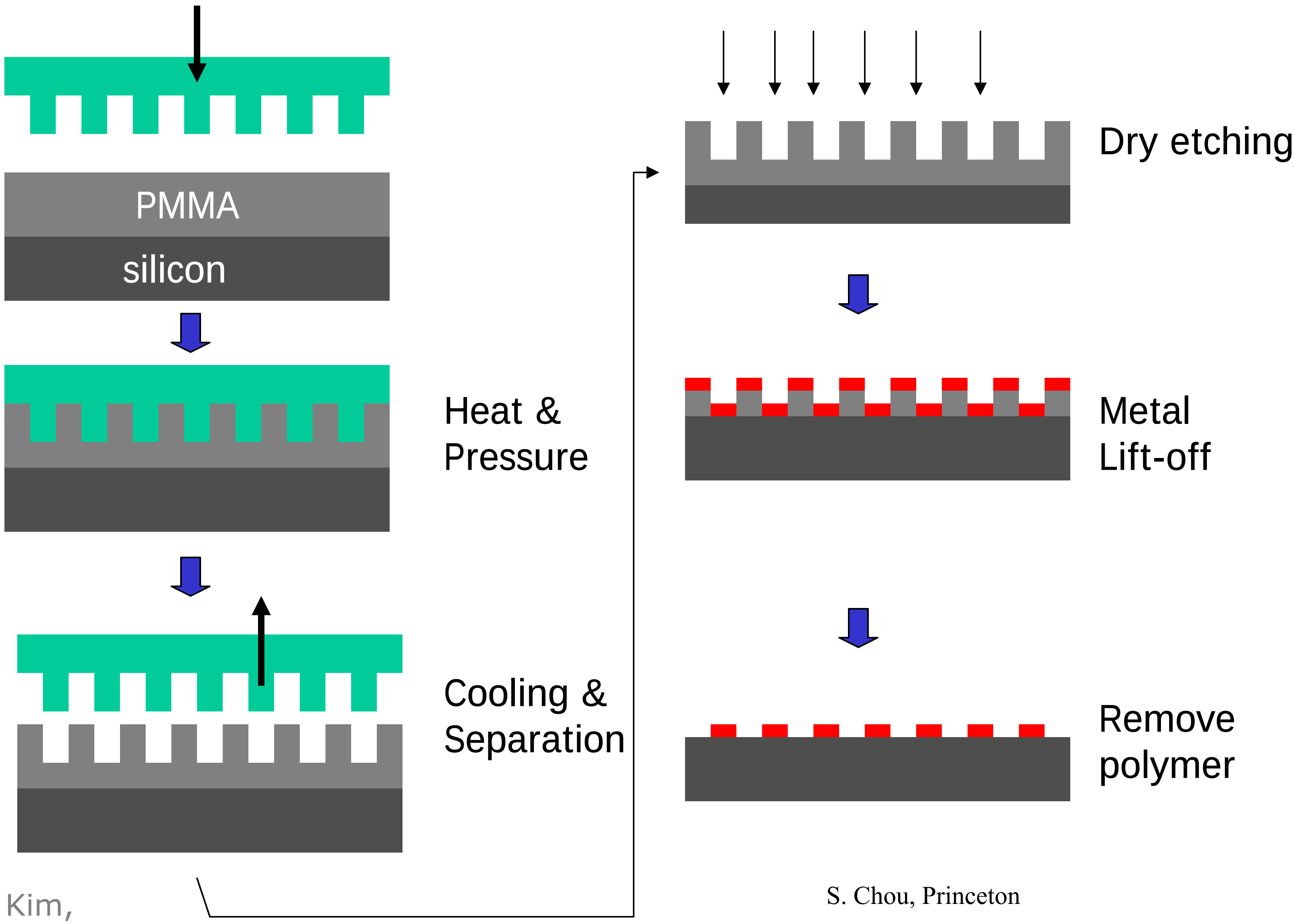
2.76/2.760 Multiscale Systems Design & Manufacturing

Fall 2004

Polymer, Protein, Complexity

Sang-Gook Kim,
MIT

Nanoimprinting



S. Chou, Princeton

Sang-Gook Kim, MIT

Nanoimprinting

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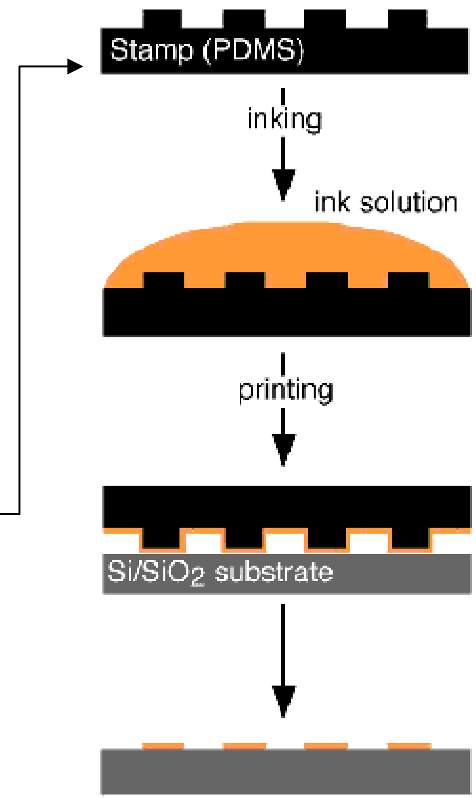
Soft Lithography: PDMS



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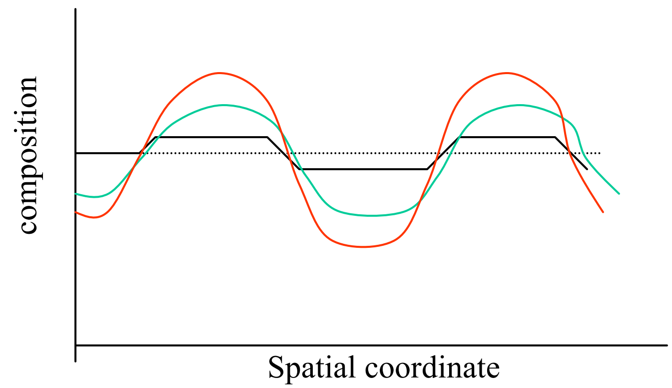
Nanopatterning by Diblock Copolymer

Diagrams and photos removed for copyright reasons.
See Park, M. et al. Science, Vol 276, 140, 1997

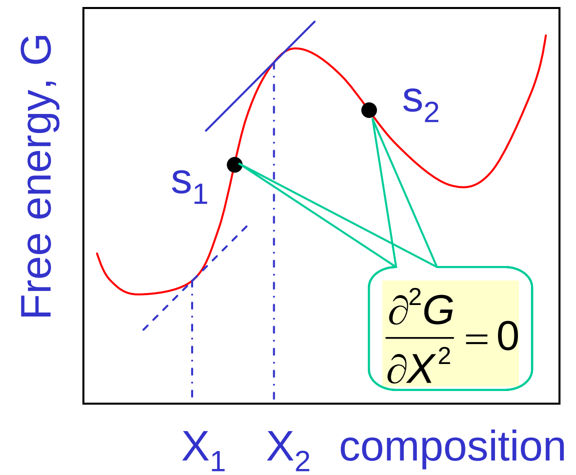
Di-block copolymers

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

$$\frac{\partial^2 \Delta \overline{G}}{\partial X^2} < 0$$



Spinodal decomposition



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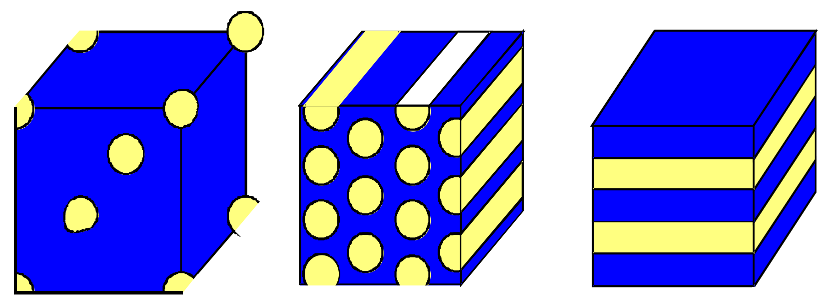
Di-block copolymer, PS-PMMA:

Diagrams removed for copyright reasons.

PS+PMMA copolymers



PMMA <10% | PMMA <30% | PMMA 50%

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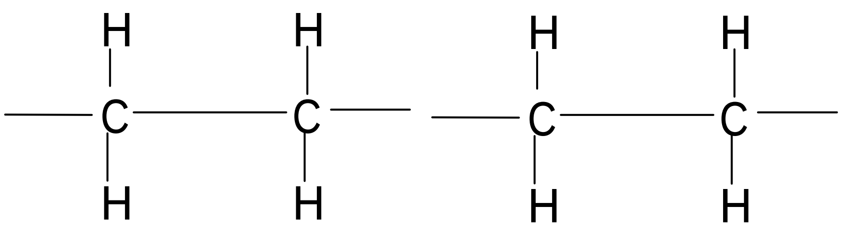
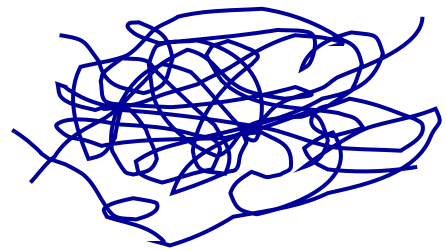
Polymers, Macromolecules

- Poly (many) + mer (structural unit)
  $-[C_2H_4]_n-$,poly[ethylene]



spaghetti



Configurational Entropy

high entropy low

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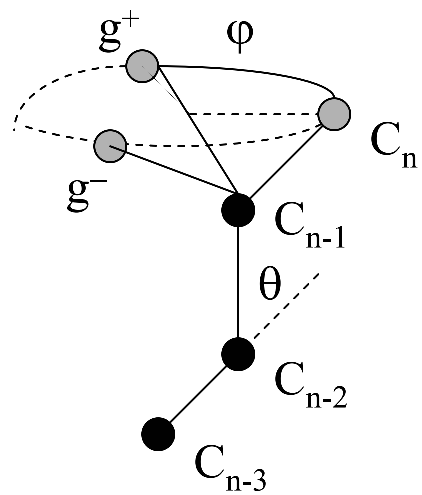
A singly bonded carbon chain

- N-2 angles

  θ, φ



$\theta = 68°$

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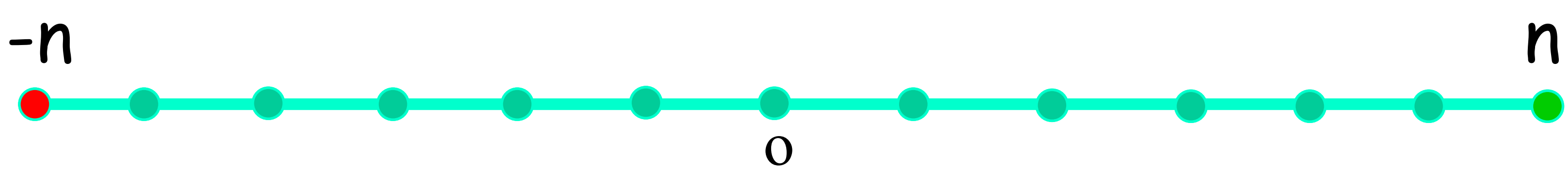
MIT

Diffusion

- Brownian motion
- Albert Einstein: Worked out a quantitative description of Brownian motion based on the Molecular-Kinetic Theory of Heat (Nobel Prize 1921)

$$\left\langle R^2 \right\rangle^{\frac{1}{2}} = \sqrt{6Dt}$$

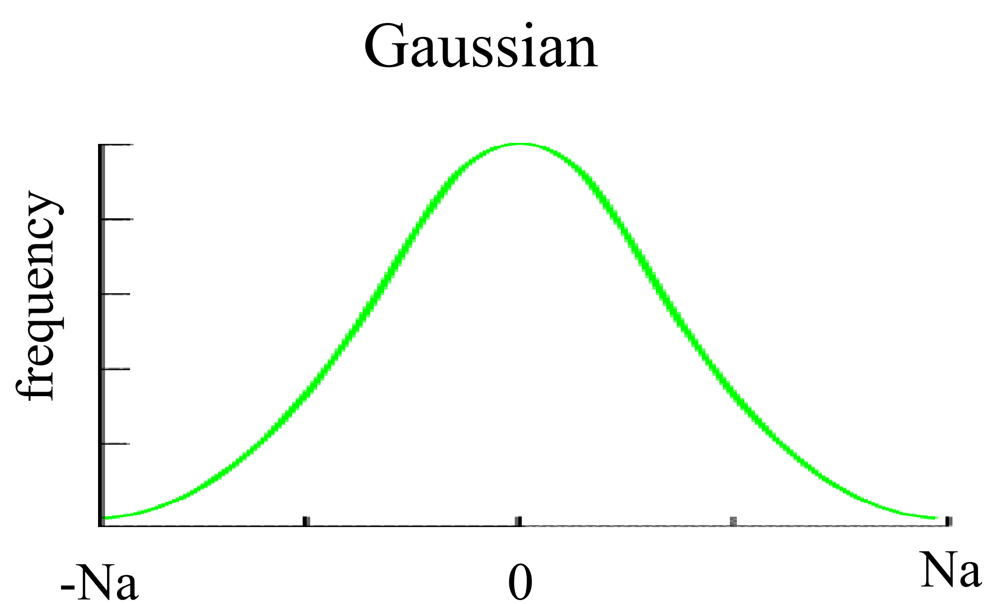
Random Walk-1D



- A simple coin toss
- Head +1 step
- Tail   -1 step
- After n steps, where you will be located?

$$\lim_{n\to\infty}\sum_{k=0}^{n}\lambda_k = 0$$

$$\text{RMS} = \sqrt{n}\,\lambda$$



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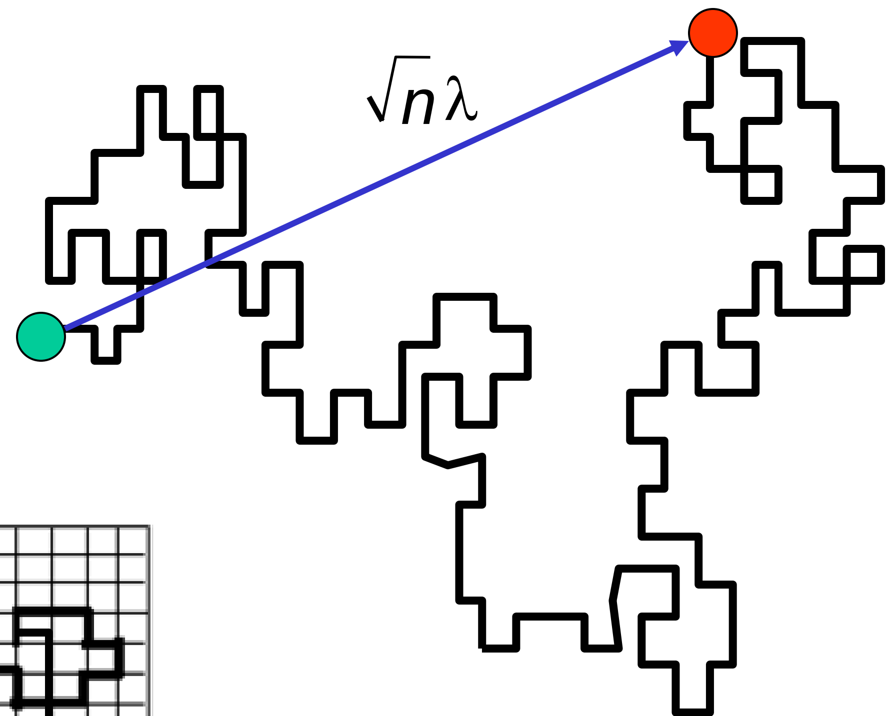
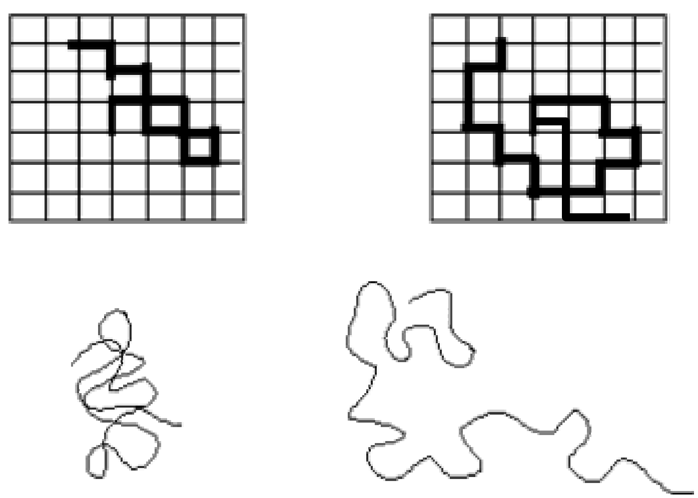
Random walk -2D

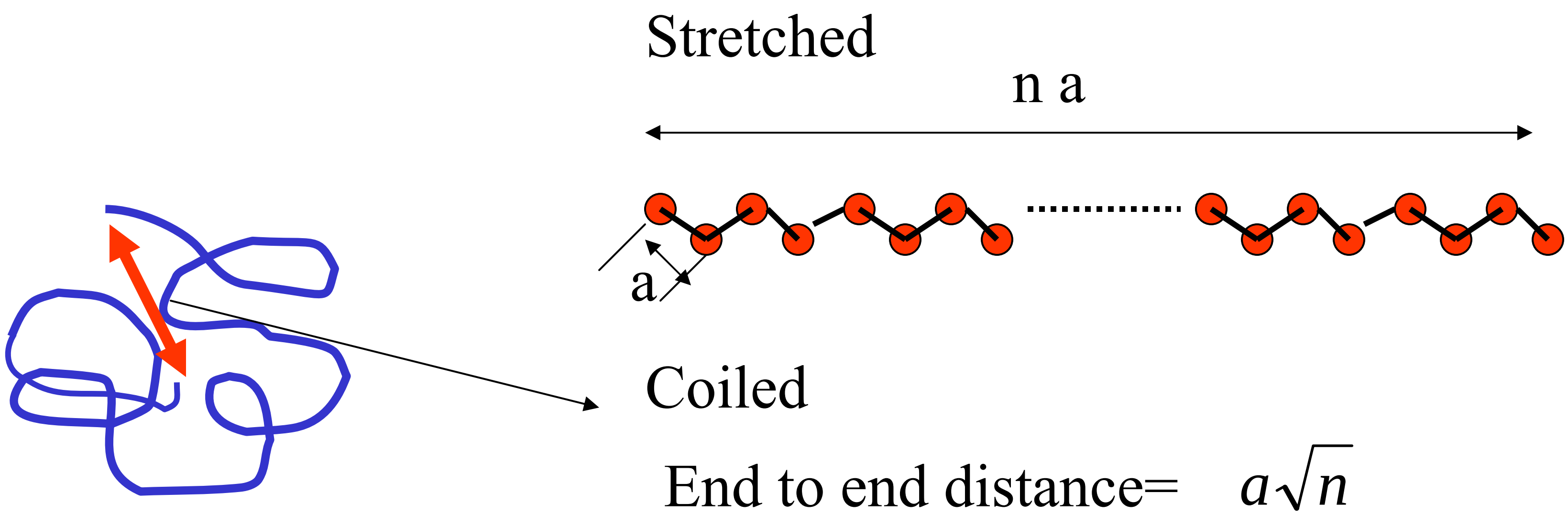
A drunkard





Entropic Behaviour

- Size & Shape of Polymer
- Configurational Entropy
- Paul Flory (Stanford): Nobel Prize 1974
- Pierre-Gilles de Gennes (Paris): Nobel Prize (1991)



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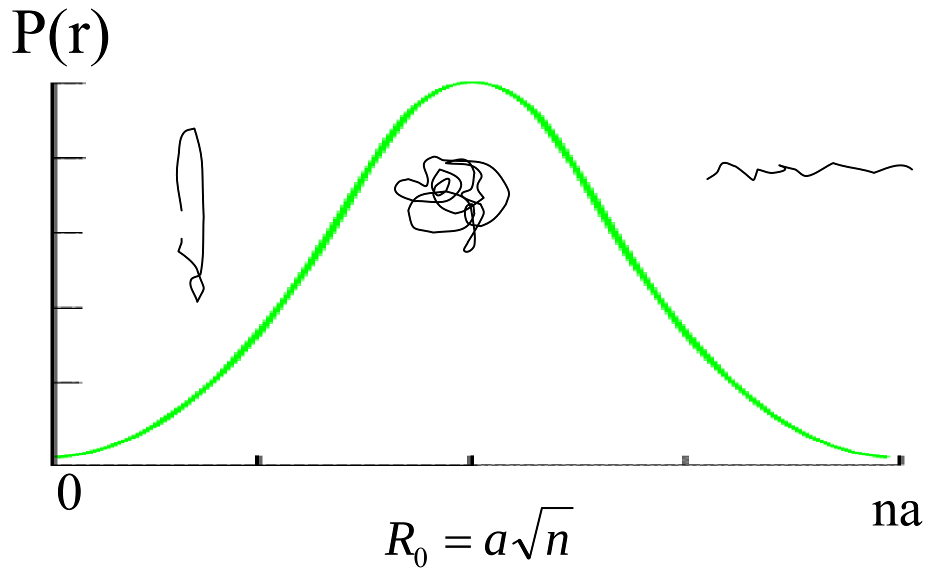
Possible Configurations

$$P(r) = \frac{1}{\sqrt{n}} e^{\frac{-r^2}{2na^2}}$$



P(r); the number of possible configurations of a random polymer coil with “n” segments of size “a” with an end-to-end distance (stretch) of r

Entropy

- Stretching the coil
- Compressing the coil

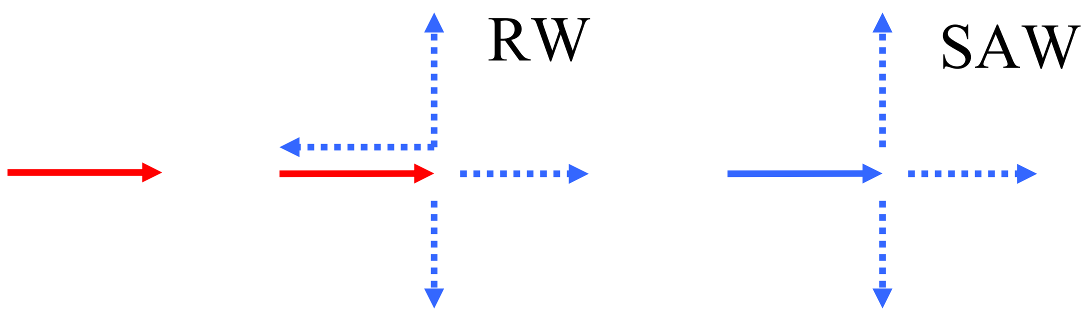
$$\Delta S = -\frac{3}{2}\left[\frac{r^2}{R_0^2} + \frac{R_0^2}{r^2}\right]$$

- Random walk of 10000 unit polymer chain of 5 Angstroms
- Length=5 micron
- Ro=5 angstroms x 100=50 nm
- Volume at the highest entropy

- Real volume is twice bigger than that of RWM.

Self Avoiding Walk

- Polymers cannot cross its own path.
- $\Delta S_{total} = \Delta S_{pressure} + \Delta S_{deformation}$



$$\Delta S = -a^3 n^2 r^{-3} - \frac{3}{2}\left[\frac{r^2}{R_0^2} + \frac{R_0^2}{r^2}\right]$$

For maximum entropy $R_0 = an^{0.6}$

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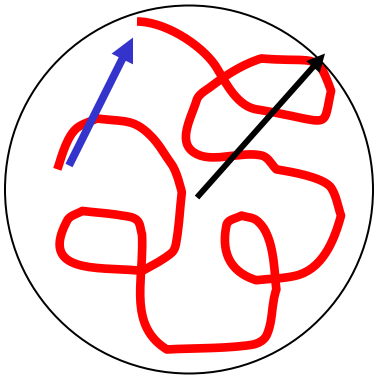
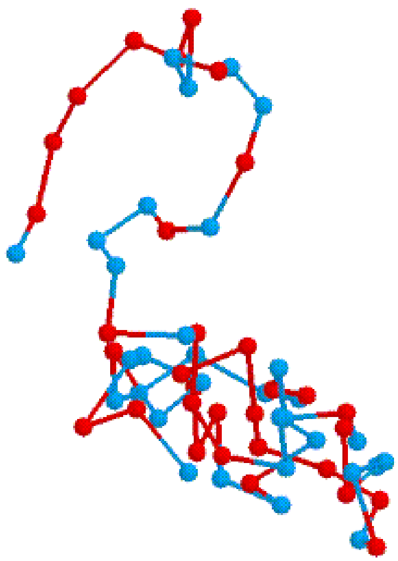
Nano-scale Phase Separation



Random walk, Gaussian distribution

e-to-e distance, R = $aN^{1/2}$
R_g = $aN^{1/2}/6$
N: number of monomers



Micro-domain periodicity, L

$$L \propto R_g \propto aN^{\frac{1}{2}}$$

N=1,000
a=5 angstroms
Then, L is around 15 nm.

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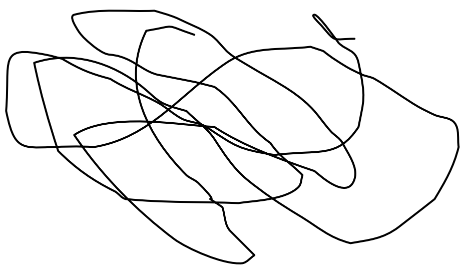
MIT

Polymers
Synthetic versus Biological

<u>Synthetic Polymer</u>

- Mostly chain like structure of repeated units (mers)
- Molecular weight distribution (chemical synthesis)
- Self avoiding walk model



<u>Protein</u>

- Primary structure exactly defined
- Fixed molecular weight
- Unique folding

Diagram removed for copyright reasons.

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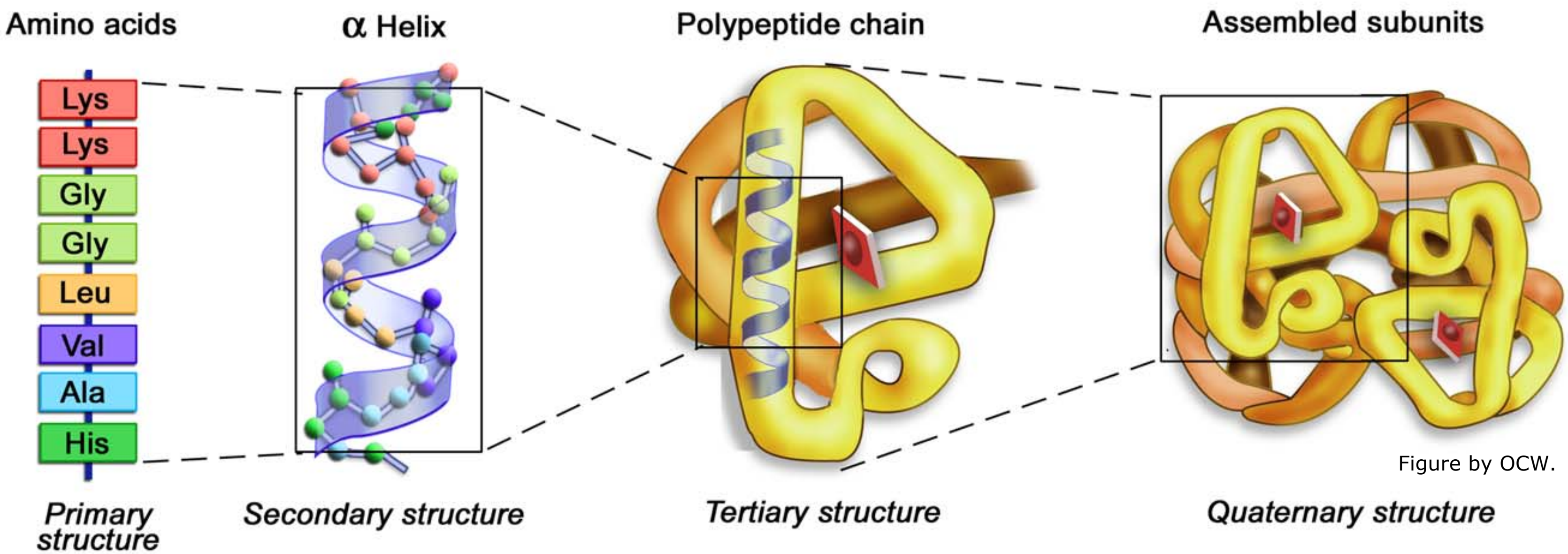
MIT

Proteins

- Proteins are polymers composed of amino acid monomers
- Proteins are characterized by a specific primary structure – order of mers in the backbone and DP
- Control of primary structure leads to control of 3D structure
- Secondary structure refers to local chain conformations – four types are known:
  - α helix – regular helix
  - β sheet – extended zig-zag
  - β turn – puts fold into β sheet
  - Globular or random coil
- Tertiary structure refers to secondary structure stabilized by H bonds – defines protein folding
- The control of protein structure builds information into the molecule that translates into function

Folding Summary



(a) Linear Sequence of peptides.

(b) Local folding into specific peptide backbone conformations.

(c) Folded 3-dimensional structure of a single polypeptide chain.

(d) Specific aggregation of two or more, identical or not, polypeptide chains.

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Common 2ndary Structures

- α helix
- β sheet
- Collagen triple helix
- Globular or random coil

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Polymers vs. Protein

- Structure formation in synthetic polymers is statistically driven.
- Structure is metastable
- Interpenetration

- Structure formation in proteins is site specific chemistry driven.
- Structure is stable
- No interpenetration
- Misfolded proteins lead to serious diseases.

What is Complexity?

DNA
~2-1/2 nm diameter

natural

Human heart

Human body
(circulatory
system)

Diagrams removed
for copyright reasons.

manmade

Carbon nanotube
~2 nm diameter

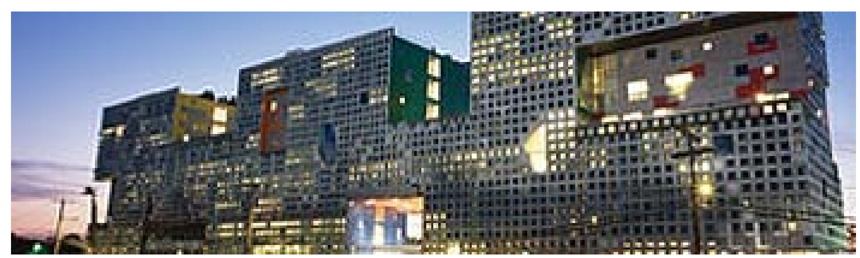
Nanotube transistor

Design for Manufacturing?

MIT Stata Center by Gehry

$300 million, 5years

MIT Simmons Hall
$ 90million, 2 years



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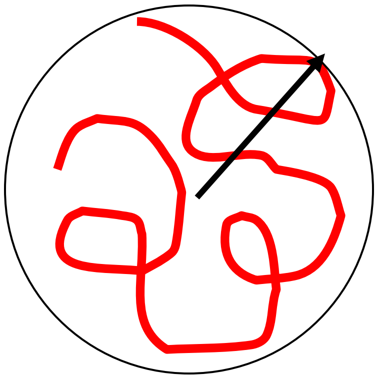
Scale Orders

$$\text{Scale order, N} = \frac{\text{size of the system}}{\text{smallest characteristic length}}$$

	N
• Cars: 5 m ←→ 500 μ	10^4
• Jig Machines: 5 m ←→ 5 μ	10^6
• Lithography M/C: 30 cm ←→ 30 nm	10^7
• Human Body: 2 m ←→ 2 nm	10^9

- Length scale of the periodicity?

Micro-phase Separation



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$R_g = aN^{1/2}/6$
N: number of monomers

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N=1,000
a=5 angstroms
Then, L is around 15 nm.

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MIT

Complex Problems

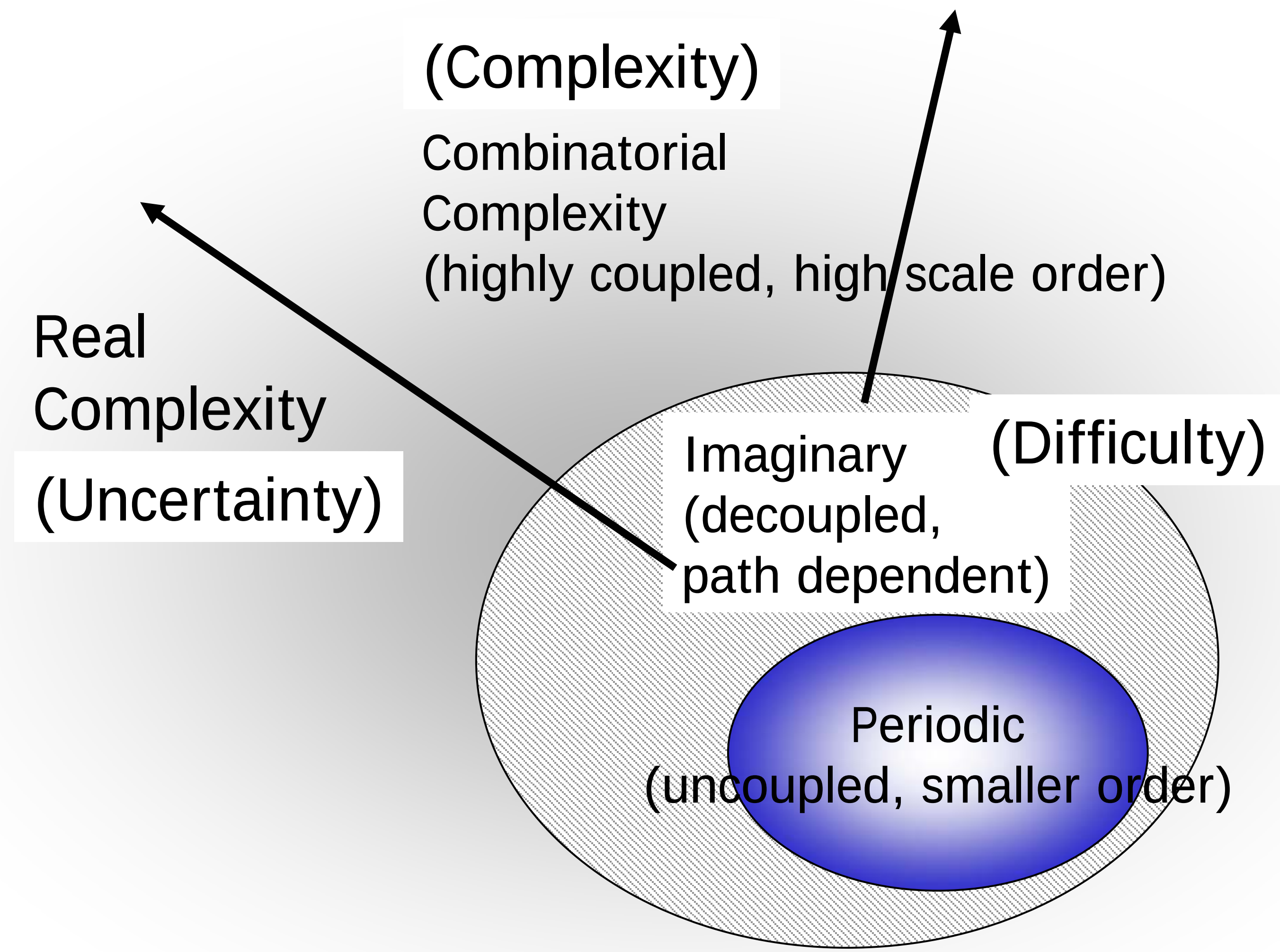
- Gaussian integrals like

$$\int D\phi e^{i\int dt \frac{dx}{dt}(t)^2}$$

- Stock market index one year from today

- Weather one year from today

Complexity Universe



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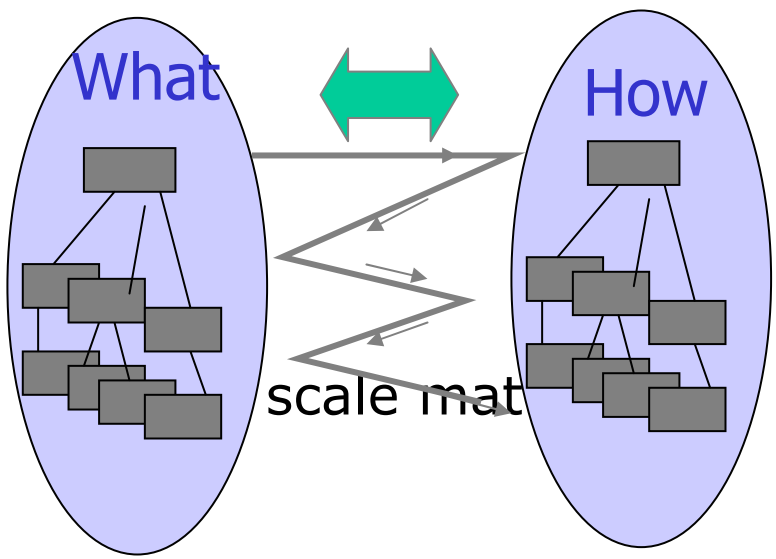
Good Design

"What" to "How"

"Top" to "Bottom"



Axiomatic approach

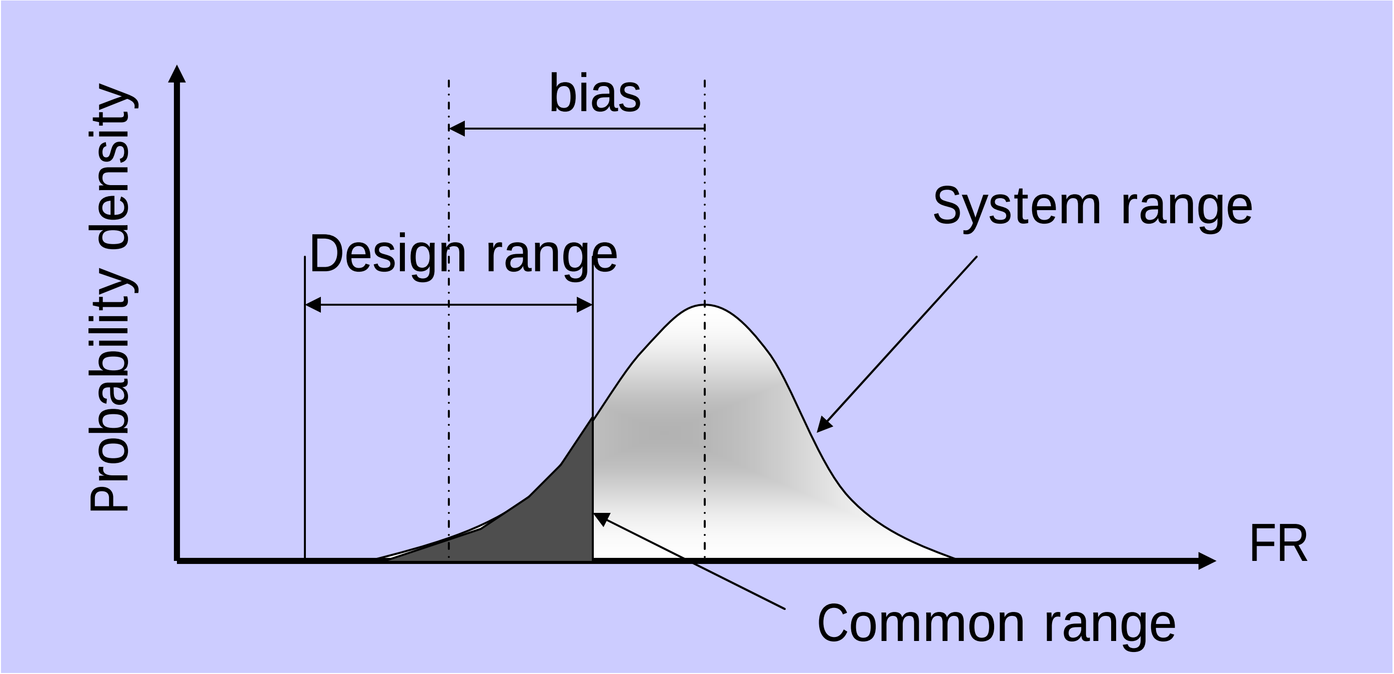
- Independence Axiom
- Information Axiom
  - Prof. Nam Suh @MIT 2.882
  - Evolution to "Complexity Theory for Nano Systems"

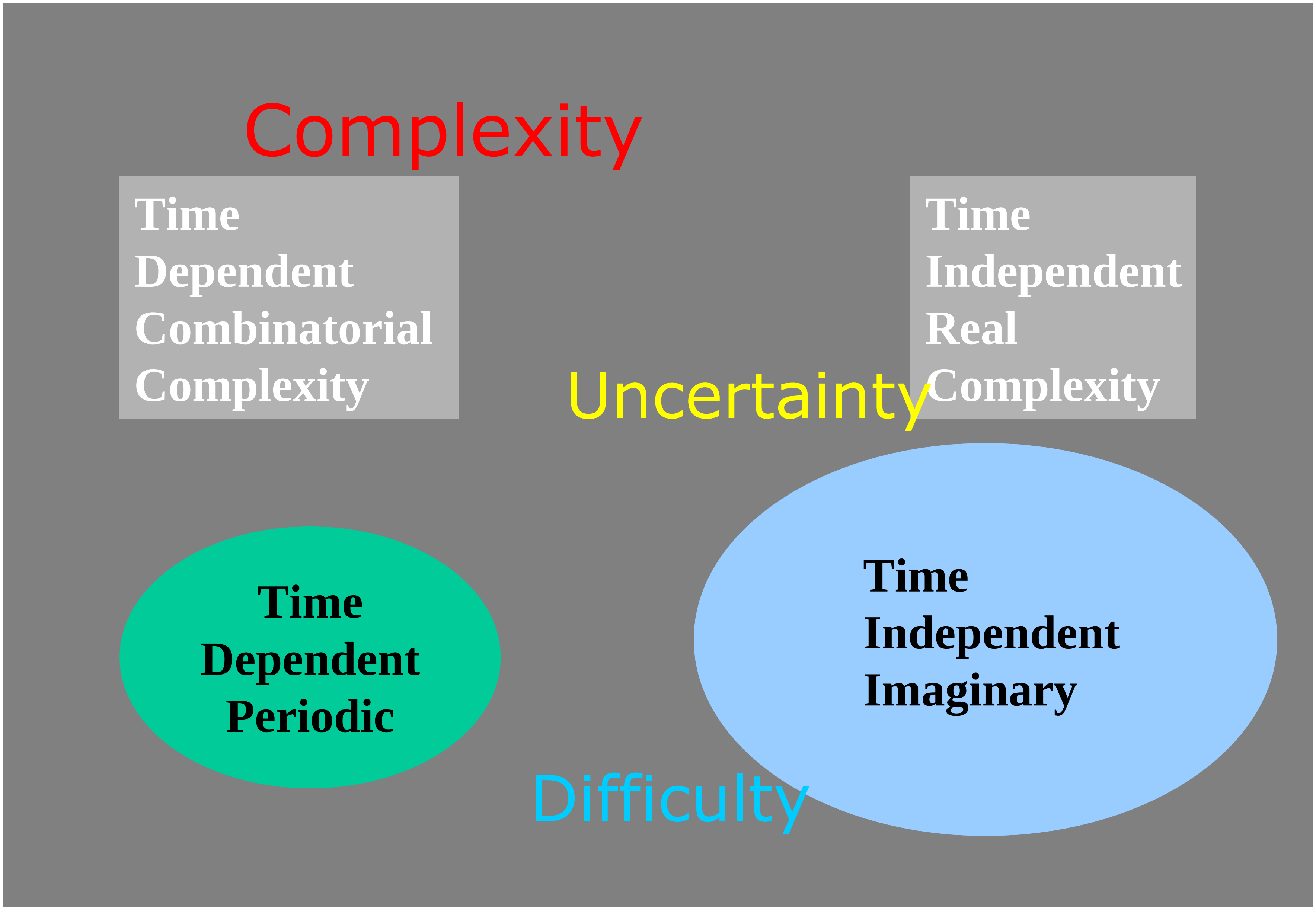
Information Axiom

- Minimize the Information Content

$$I = \log_2 \frac{1}{P} = -\log_2 P$$

P : Probability of success =common range/system range





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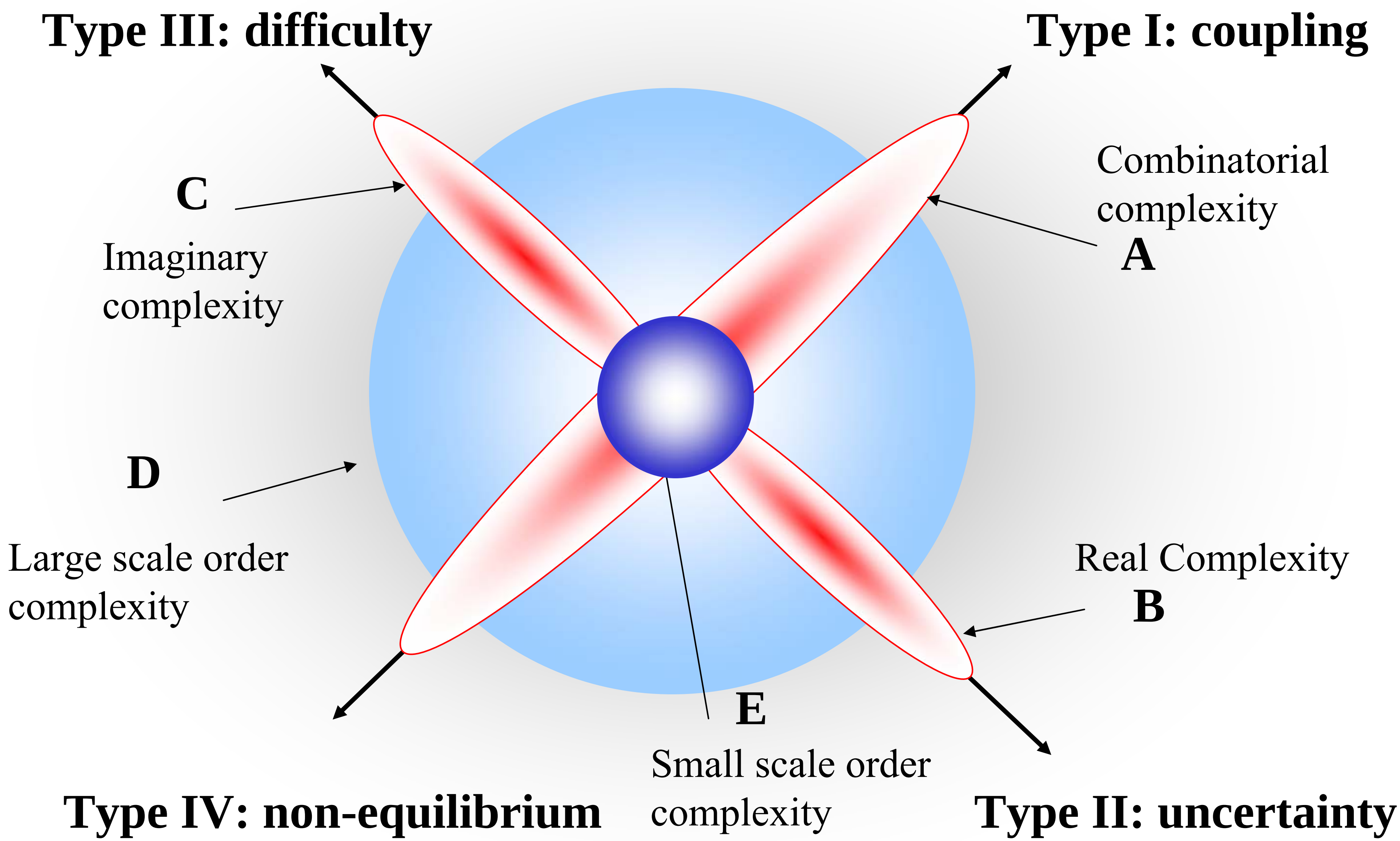
Causality of Complexity



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Complexity

A system is complex when;

- A design is coupled.
- System ranges vary with time.
- The outcome is uncertain. (low probability of success)
- The scale order is very high. (over 10^9)

Complexity can be reduced by;

- Periodic functions (temporal, spatial, etc.)

Functional Periodicity

- Time indepenedent real and imaginary complecity.
- Time dependent combinatorial and periodic complexity.
- Time dependent combinatorial complexity can become periodic complexity by functional periodicity. [Suh, MIT]

  – Temporal
  – Geometrical
  – Biological
  – Manufacturing process
  – Chemical information
  – Circadian
  – etc.

Multi-scale system assembly by periodic building blocks?

- Periodic micro-domains
- Functionally uncoupled domains
- Periodicity,
- Nano to Macro
- Biomimetic?

Tendon hierarchy

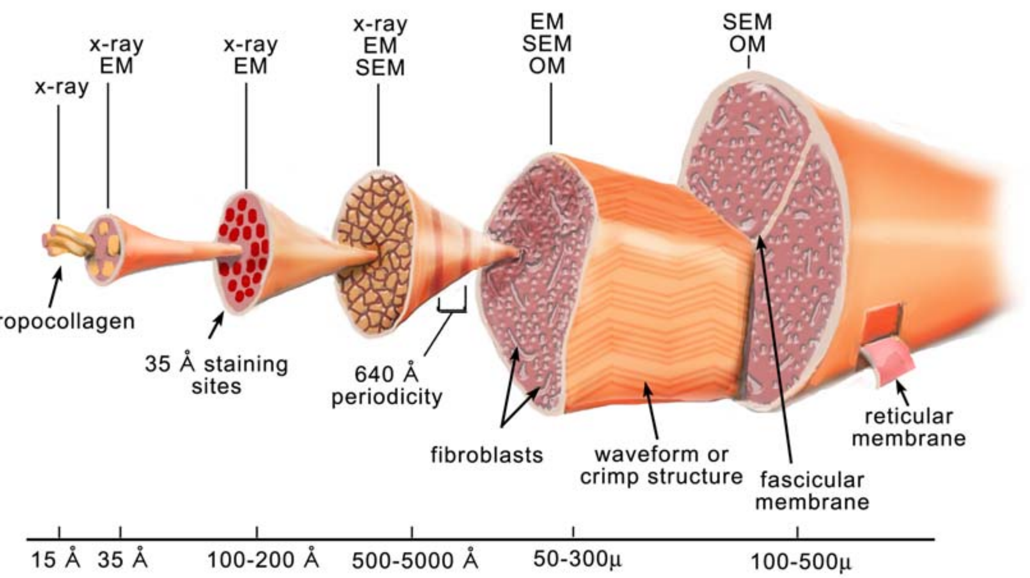

Figure by OCW.

MIT Simmons Hall

$$L \propto R_g \propto aN^{\frac{1}{2}}$$

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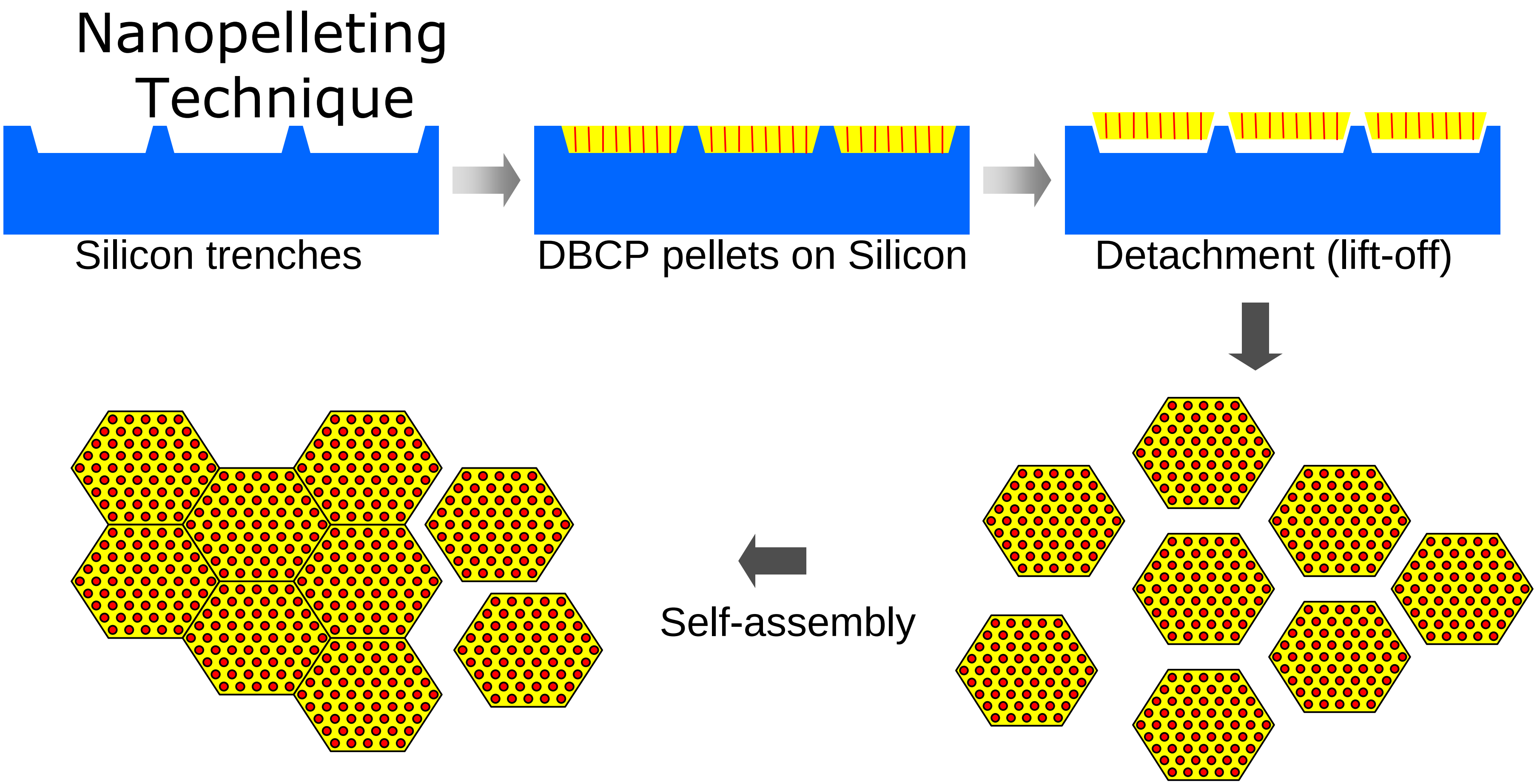
Block Assembly



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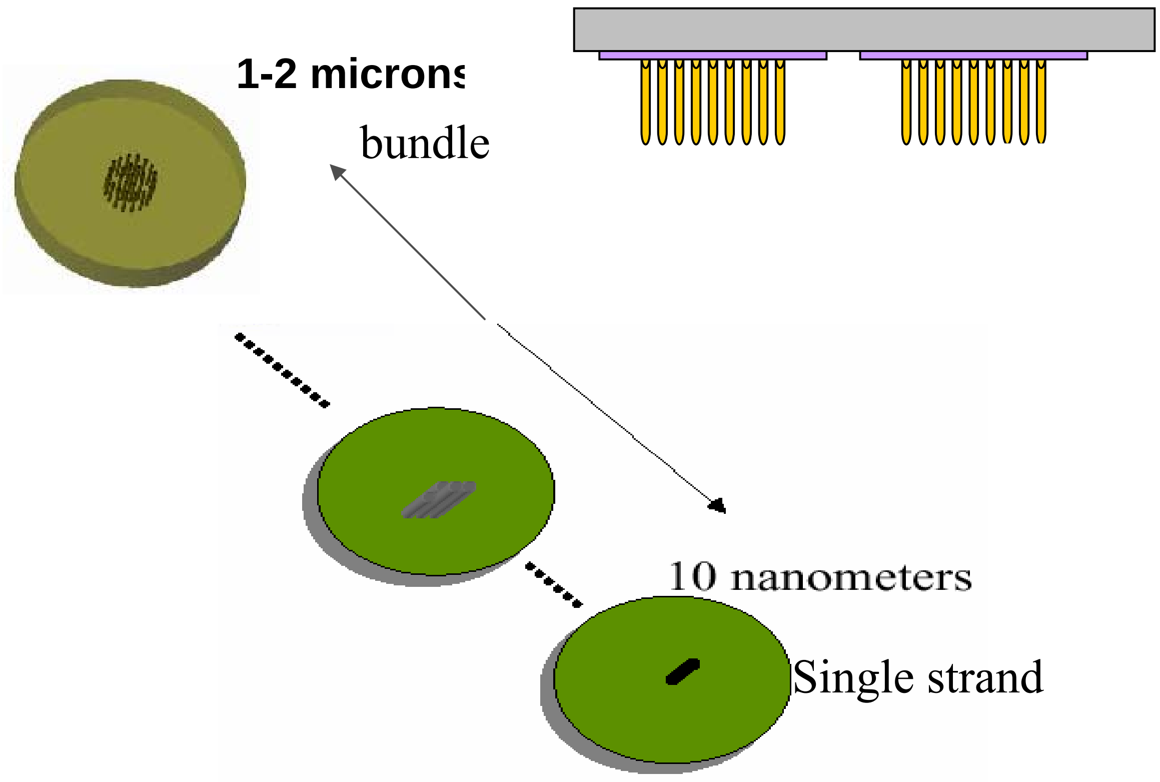
Bundle CNT nanopellet CMPed and Transplanted

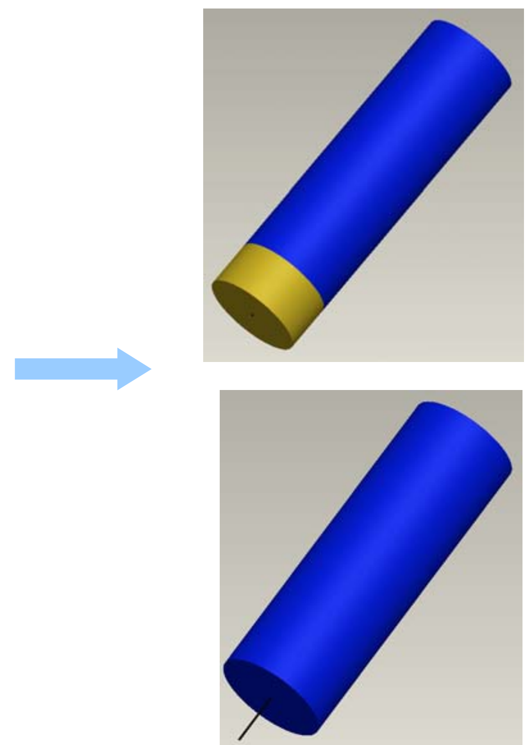
Photos removed for copyright reasons.
See T. El-Aguizy, J-h Jeong, Y. B. Jeon, W. Z. Li, Z. F. Ren and S.G. Kim, "Transplanting Carbon Nanotubes", Applied Physics Letters, Vol 85, No. 25, P.5995, 2004

High aspect ratio nanopellets

Cold cathode array,
FED, Data storage,
Multi-E-beam array for NGL



Nanocandles



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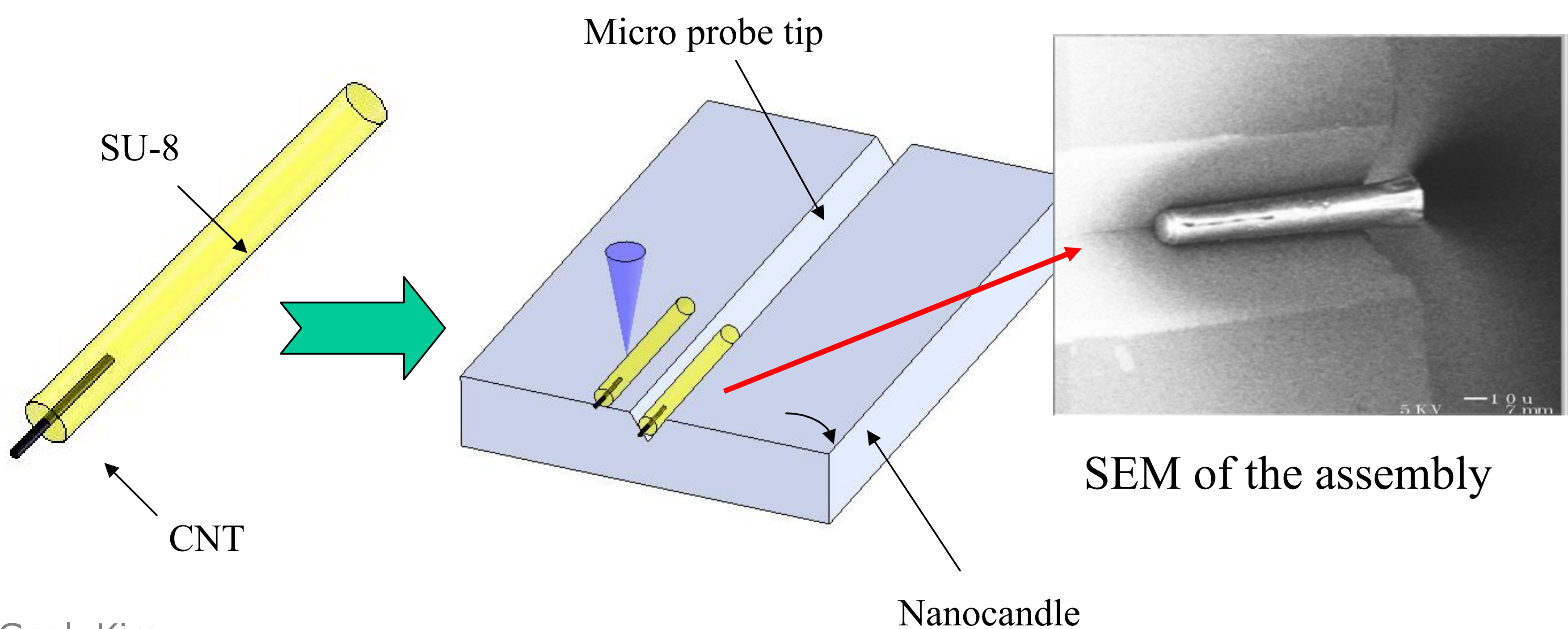
In-Plane Assembly of High-Aspect Ratio Nanocandle

- Mechanical in-plane assembly of nanocandle in the V-groove with a micro probe tip
- Bonding of nanocandle in the V-groove with a drop of epoxy



SEM of the assembly

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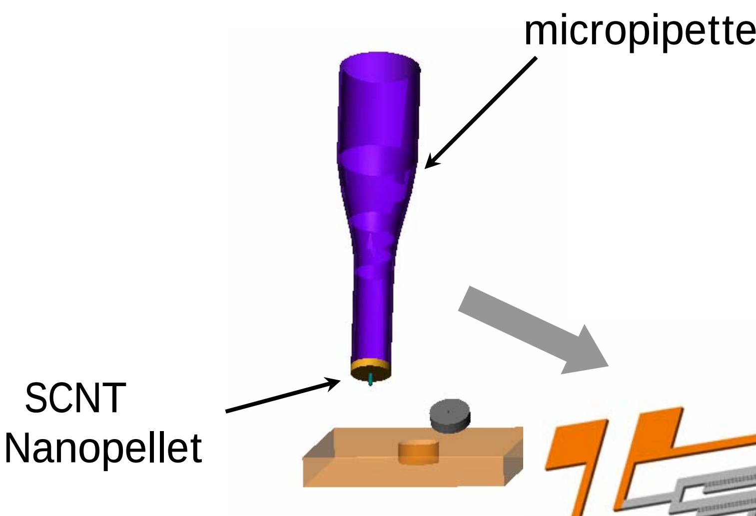
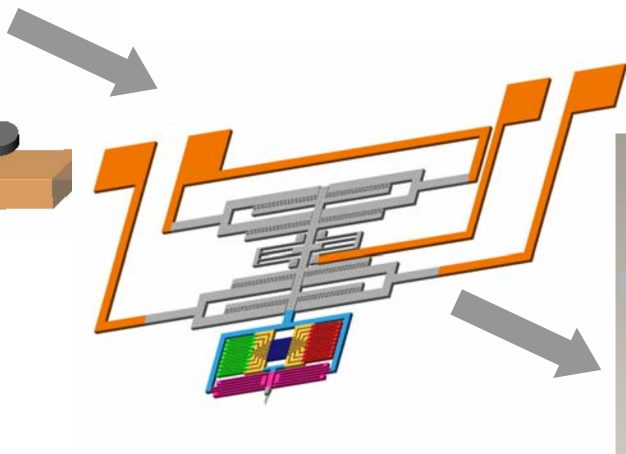
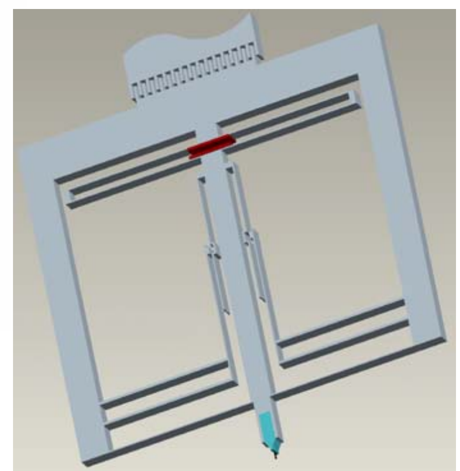
MIT Nanopipette

- Nanotube assembly to the tip of a micropipette



- Nanotube assembly to the tip of an in-plane AFM
  - Parallel Imaging and Pipetting
  - Multi-energy probing
  - Manufacturable
  - Arrayable





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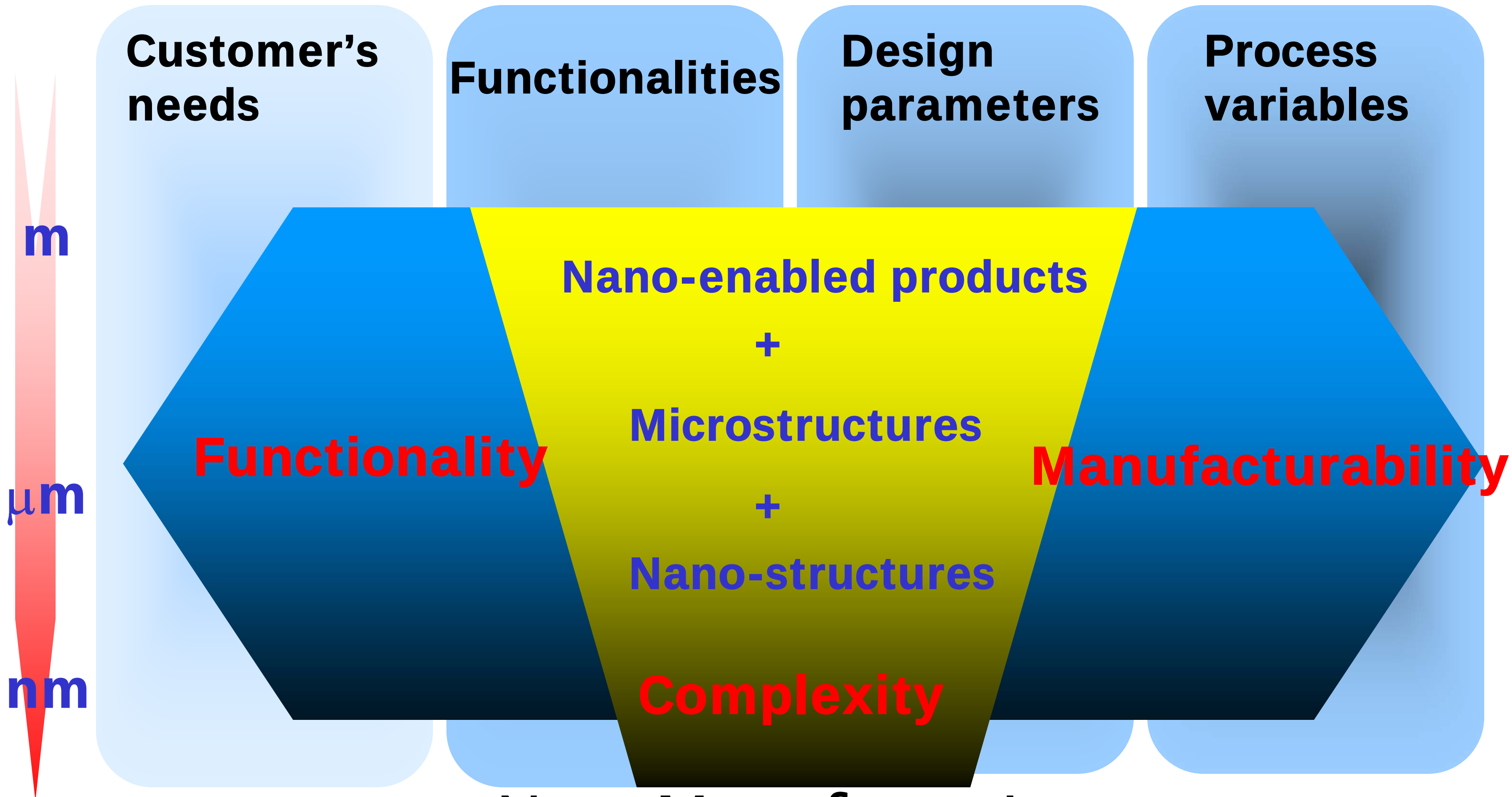
A multiscale system design…



NanoManufacturing

Sang-Gook Kim, MIT